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SPECIFICS OF DEPOSITING FUNCTIONAL COATINGS IN FLOAT-GLASS PRODUCTION

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The specifics, advantages, and technological parameters of producing reflective and low-emission glasses using pyrolytic methods in the course of float glass production are considered.

The market for large-size construction glass with film coatings has grown intensely lately. At the same time, requirements imposed on architects and builders with respect to effective use of thermal energy and reducing heat losses via light-transmitting glazing in buildings are getting more stringent.

Reflective and low-emission glasses currently belong to most efficient types of energy-saving glazing. All leading glass manufacturers in the world produce such glass. According to the data of foreign companies, the share of energy-efficient glazing in Europe is about 50%, in the USA up to 30%. The estimated potential Russian market is at least 35 million m² per year [1].

Film glasses produced in the course of float glass production using chemical (pyrolytic) methods have been present on the market for years and are used as sun-shielding and low-emission glazing.

The development and large-scale use of chemical (pyrolytic) methods for depositing coatings has become accessible with the development of the float process and organometallic technologies. The most common lately are the vapor-phase and the powder methods for depositing oxide and metal coating on a glass ribbon.

The technological scheme of the pyrolytic methods for depositing functional coatings includes the following main processes [1]:

- preparation of the film-forming reactant;
- applying the coating to a glass ribbon;
- ventilation and purification;
- annealing, cutting of film glass.

The specifics of depositing coating on a glass ribbon consist mainly of selecting the film-forming reactants, the method and equipment for coating deposition, and the removal of waste reactants from the reaction zone (RF patent No. 2087437) [1, 2].

The main requirements imposed on film-forming reactants are as follows:

- ensure formation of a coating with preset optical characteristics;
- the pyrolysis temperature and the rate of decomposition of reactants have to create conditions for the formation of optically homogenous defect-free coatings without inclusions of pyrolysis products (soot, etc.) on a glass ribbon produced at a velocity of 300 m/h.

To obtain reflective and low-emission coatings (oxide, metallic), different films have to be deposited.

In the first case, these are mainly oxides of transitional metals with a refractive index greater than 2, such as oxides of iron, cobalt, chromium, titanium, etc., as well as some metals, such as silicon, ensuring reflection of IR rays in the solar wavelength range. It should be noted that normally various combinations of organometallic oxide compounds are used in the preparation of film-forming solutions. This is needed to attain a required level of light transmission and reflection of the solar spectrum by glass, as well as improve their service characteristics, mainly adhesion and strength parameters.

Glass with a low-emission coating is usually produced by depositing mainly semiconductor tin oxides modified by nitrogen, fluorine, antimony, and indium compounds on a glass ribbon by means of pyrolysis. The modifiers are introduced into the oxide to disturb its stoichiometry, in order to raise its conductivity and, accordingly, improve the heat-reflecting properties of glass in the wavelength range of $7-14 \, \mu m$

The film-forming compounds used to form the specified functional coatings on a glass ribbon during its production are organometallic compounds of iron, cobalt, chromium, titanium, nickel, and tin having a high rate of decomposition and good spreading capacity. The temperature interval for the pyrolysis of organometallic compounds $(300-600^{\circ}\text{C})$ is

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| Conditions of feeding components to the evaporation chamber | | | | | Conditions of additional correction of film-forming reactant | | | |
|-------------------------------------------------------------|---------------------------------------------|-------------|-----------------------------------------|-----------------------------------------------|--------------------------------------------------------------|----------------------|-------------|------------------------------------------------|
| Film-forming compound | solution solution feed temperature, °C kg/h | solution | carrier gas feed rate, liters/min | content of film- forming reactant, % | reactant temperature, °C | feed rate, liter/min | | content |
| | | | | | | O_2 | water steam | of organometallic compound in mixture, % |
| Organometallic compounds | 21 – 570 | 0.25 - 0.54 | 100 – 400 | 12 – 16 | _ | _ | _ | _ |
| Dichlorodimethyl-tin | 138 | 29 | 250 | 16 | 160 | 50 | 23 | 13 |

compatible with the glass ribbon temperature in the zone of coating application.

Various combinations of oxides can be obtained either using mixtures of organometallic compounds, or coprecipitated organometallic compounds in prescribed ratios. The latter are preferable since they allow for more precise control of the composition and stoichiometry of coatings deposited.

Organometallic compounds widely used in technological processes are compounds of the chelate type, especially acetylacetonates of transitional metals, as well as other compounds, such as tin dibutyl fluoride, triethyltin, diethyldichlorosilane, etc.

Different companies use various equipment for the vapor-phase and powder methods, especially coating-application units. Since technological equipment is placed above the glass ribbon, or between the melting tank and the annealing zone, or inside the melting tank and is used for spraying metal-organic compounds, stringent requirements are imposed on the constancy of the temperature of the equipment and the glass ribbon in the coating-application zone, on the uniform concentration of the film-forming agents in the coating-application chamber, etc. (RF patents Nos. 2039020, 2062258, and 2087437).

This equipment has a complicated design and requires strict compliance with technological regulations in operation.

Thus, for the vapor-phase method the usual equipment includes a chamber for evaporation and conversion of the film-forming agent into a vapor phase, a device for introducing the carrier gas, homogenization of the vapor mixture, sprayer for depositing film-forming reactants on the glass ribbon, and equipment for the removal of the reaction products from the spraying zone. Special requirements are imposed on the constancy of the temperature of equipment, reactants, and the glass ribbon (RF patent No. 2087437).

The powder method requires a complicated set for coating deposition (RF patent No. 2062258). It usually contains a unit for the formation of a powdered flow of film-forming material in a gas suspension near the glass ribbon, homogenization of its concentration, acceleration of the gas flow near the glass ribbon, and equipment ensuring uniformity of coating deposition.

The technological parameters for depositing film-forming reactants using the vapor-phase method (RF patent No. 2062258) are given in Table 1.

The coatings are deposited on a glass ribbon within temperature intervals of 593 - 732 and 400 - 565°C, depending on the type of the reactant used. The rate of the coating thickness increment on glass is approximately 2200 Å/sec.

Technological parameters for depositing coatings using the powder method (RF patent No. 2039020)

| Film-forming compounds Organometallic compounds of transitional metals |
|----------------------------------------------------------------------------------------------------------------------------------------|
| Granulometric composition, μm 5 – 40 |
| Flow rate of material per 1 m |
| of nozzle length, kg/h |
| Gas flow rate per 1 m of nozzle length, m ³ /h |
| primary |
| secondary |
| Quantity of powder injected, kg/h 24 |
| Coating width from the first injector, mm $50-150$ |
| Rate of depositing powder on glass ribbon, m/sec $.25-60$ |
| Distance between the sprayer |
| and the glass ribbon, mm $\dots \dots \dots$ |
| (preferably 30 - 90) |

The main advantages of the chemical methods for depositing coatings on a glass ribbon are as follows:

- compatibility with highly efficient glass-production process (float process);
- absence of additional operations of preparing glass surface for applying coating;
 - possibility of fast renewal of the product range;
- good service parameters of film glasses (adhesion strength, durability);
 - possibility of using film glass in single-pane glazing;
- various options of further treatment (hardening, bending).

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